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(54) Title of the Invention: Hot-melt adhesive compositions

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## SPECIFICATION

### 1. Title of the Invention

Hot-melt adhesive compositions

### 2. Scope of the Patent Claim

1. A hot-melt adhesive composition, characterized in that it contains the three components indicated below.

- (A) A copolymer obtained by the hydrogenation of a styrene-isoprene-styrene block copolymer or styrene-butadiene-styrene block copolymer
- (B) Tackifier
- (C) Crystalline polypropylene of number average molecular weight not more than 20,000.

### 3. Detailed Description of the Invention

#### (a) Purpose of the Invention

##### Industrial Field of Application

The invention concerns hot-melt adhesive compositions which have an excellent adhesive strength on polyolefin-based resins and metals for example and excellent durability of adhesion such as heat resistant adhesion and thermal-creep resistance, and excellent stability when heated and melted which can be used in a wide variety of industrial applications in various industrial fields starting with the bonding of electrical parts.

##### Prior Art

In the past dimer acid-based polyamide adhesives have been widely used as hot-melt adhesives which have excellent heat resistance when bonding chiefly metal materials in the bonding of electrical parts such as when fixing television yokes, when sealing industrial filters and when bonding together parts used in automobiles for example.

However, these polyamides have a disadvantage in that they are subject to thermal deterioration due to the amide groups when they are being melted by heating, in that the adhesives require pre-heating and in that their resistance to cold is poor. Moreover, they have a serious weakness in that they have no bonding power with

plastics such as the polyolefin resins which are now being widely used in such applications.

Furthermore, other hot-melt adhesives which have been investigated include those in which ethylene-vinyl acetate copolymers, ethylene-ethyl acrylate copolymers and atactic polypropylene for example, are used, but with all of these the properties such as the adhesion heat resistance, cold resistance and adhesion properties on polyolefin resins, for example, are still not realized satisfactorily.

#### Problems to be Resolved by the Invention

The present invention provides hot-melt adhesive compositions which overcome the abovementioned difficulties experienced with the conventional hot-melt adhesives and which have excellent adhesion properties with metals and with plastics, starting with the polyolefins such as polypropylene and polyethylene which were known as materials which are difficult to bond, and which have heat resistance and cold resistance and which have excellent operability and stability on being heated and melted in melt coating apparatus as hot-melt adhesives.

#### (b) Constitution of the Invention

##### Means of Resolving These Problems

As a result of a further thorough investigation of compositions which provide superior hot-melt adhesives which are free of the problems outlined above, the inventors have discovered that compositions which contain the three specified components satisfy these requirements, and the invention is based upon this discovery.

Thus, the present invention is a hot-melt adhesive composition, characterized in that it contains the three components indicated below.

- (A) A copolymer obtained by the hydrogenation of a styrene-isoprene-styrene block copolymer or styrene-butadiene-styrene block copolymer
- (B) Tackifier
- (C) Crystalline polypropylene of number average molecular weight not more than 20,000.

The hot-melt adhesives obtained from such compositions have excellent adhesion heat resistance and thermal creep resistance on polyolefin resins and polypropylene in particular and also on metals, and they have an excellent performance

in terms of operability and thermal stability on being heated and melted in melt-coating apparatus.

(A) The Copolymer Obtained by Hydrogenating Styrene-Isoprene-Styrene Copolymer or Styrene-Butadiene-Styrene Copolymer

The copolymers used in the invention are generally called SEBS-based thermoplastic elastomers, and they include commercial products such as, for example, Clayton G-1650, Clayton G-1652 and Clayton G-1657 produced by the Shell Chemical Co.

Copolymers which have not more than 35 wt% of styrene units are preferred as the copolymers which are used in this invention.

The proportion of such copolymer compounded in a composition of this invention, as a ratio by weight, is preferably from 5 to 70 wt% of the composition, and with less than 5 wt% the adhesive strength on polyolefin-based resins and especially on polypropylene, and also on metals, falls, while an amount in excess of 70 wt% may not only reduce the adhesive strength but also adversely affects the fluidity when the adhesive is being heated and melted, and this is undesirable. More desirably, the amount compounded is from 10 to 50 wt% and, depending on the amount which is used, it is possible to obtain compositions which have excellent bonding properties which are very strong.

(B) Tackifier

Natural rosin, polymer rosin and derivatives thereof, such as pentaerythritol ester rosin and glycerine ester rosin, and hydrogenated resins derived therefrom, can be used as rosin-based tackifiers, and actual examples of commercially available products include Gum Rosin, Wood Rosin, Ester Gum A, Ester Gum Rosin H, Bensel A and Bensel C (produced by the Arakawa Kagaku Co.) and Bentarin A, Foral AX, Foral 85, Foral 105 and Bentarin C (produced by the Rika Hercules Co.). Furthermore, terpene-based tackifiers which can be used include polyterpene-based resins, terpene-phenol-based resins and hydrogenated forms of these resins, and actual examples of commercially available products include Pikolite S and Pikolite A (produced by the Piko Co.) and YS resin, YS Polystar-T and Clearron (produced by the Yasuhara Yushi Co.).

Moreover, there are also petroleum-resin-based tackifiers, such as aliphatic petroleum resins, aromatic petroleum resins, copolymer petroleum resins and hydrogenated petroleum resins, and actual examples of commercially available products include Escorex (produced by the Tonen Sekiyu Kagaku Co.), Hirex (produced by the Mitsui Sekiyu Kagaku Co.), Kuinton (produced by the Nippon Zeon Co.), Wintak (produced by the Goodyear Co.), Statack (produced by the Rhinehold Co.), Tohopetrojin (produced by the Tonen Sekiyu Kagaku Co.), Nisseki Neopolymer (produced by the Nippon Sekiyu Kagaku Co.), Petrojin and Tackace (produced by the Mitsui Sekiyu Kagaku Co.), Escorex (produced by the Esso Co.), Toho High Resin (produced by the Toa Sekiyu Kagaku Co.), Supertack (produced by the Rhinehold Co.) Arkondo and M (produced by the Arakawa Kagaku Kogyo Co.) and Pikobear (produced by the Oiko Co.). Moreover, chroman-indene resins and thermoplastic phenol resins, for example, can also be used. In this invention these tackifiers can be used in accordance with the application, but the hydrogenated resins are especially desirable in this invention. These tackifiers are used to improve the bonding properties on the materials which are being bonded.

The amount of such tackifier compounded in a composition of this invention, as a ratio by weight, is preferably from 10 to 70 wt%, and most desirably from 20 to 60 wt%. If this ratio is less than 10 wt% then the bonding properties on adherends such as polypropylene in particular and metals are adversely affected while conversely if it exceeds 70 wt% the cohesive strength of the adhesive is reduced and there is a danger that the bonding strength and especially the bonding heat resistance will fall. Tackifiers which have a softening point of at least 60°C and not more than 150°C are especially desirable in this invention.

(C) Crystalline Polypropylene of Number Average Molecular Weight Not More Than 20,000

The crystalline polypropylene of which the number average molecular weight is not more than 20,000 is a powder-like polypropylene which has been obtained by polymerizing propylene or degrading isotactic polypropylene, and actual examples of commercially available products include Viscol 330P (number average molecular weight 15,000, R & B softening point 152°C), Viscol 550P (number average molecular weight

4,000, R & B softening point 150°C), Viscol 660P (number average molecular weight 3,000, R & B softening point 145°C), Viscol TS-200 (number average molecular weight 3,500, R & B softening point 145°C) (all produced by the Sanyo Kasei Co.).

Compositions with little tack which have excellent adhesion properties and especially adhesion heat resistance on adherends and excellent fluidity on heating and melting can be obtained with such polypropylenes. Moreover, if a crystalline polypropylene of molecular weight from 1,000 to 5,000 is used then these characteristics are even better, and the use of polypropylenes of this type is preferred in the invention.

The proportion of such polypropylene compounded in a composition of this invention is, as a ratio by weight, from 10 to 75 wt%, and most desirably from 20 to 60 wt%. If this ratio is less than 10 wt% then there is a danger that the adhesive strength on polyolefin-based resins and especially polypropylene, and on metals, will fall, and the fluidity when melted may be unsatisfactory, while if it exceeds 75 wt% then the adhesion properties and adhesion heat resistance again tend to become inadequate in the same way.

In this invention, some of the abovementioned crystalline polypropylene can be replaced with a non-crystalline atactic polypropylene which has been isolated as a by-product of isotactic polypropylene in the main, such as, for example, Vistarol (R & B softening point 125 to 155°C, produced by the Chiba Fine Chemical Co.), Vistack L (R & B softening point 50 to 60°C, produced by the Chiba Fine Chemical Co.) and Tack B33 (R & B softening point 140 to 160°C).

Moreover, if the extent of such replacement is 70 wt% or more of the crystalline polypropylene then the characteristics of the crystalline polypropylene are lost and so the replacement of 70 wt% or more must be avoided.

Moreover, polypropylene in which other monomers have been copolymerized within the range where the crystallinity is not lost can also be used for the crystalline polypropylene of this invention.

#### Other Additives

The compositions of this invention comprise the aforementioned hydrogenated block copolymer, tackifier and polypropylene and as a result they have excellent

compatibility when heated and melted and they also have the excellent adhesive characteristics described earlier, and in those cases where EVA, EEA, gelled EVA, ethylene-propylene copolymer, styrene-isoprene-styrene or styrene-butadiene-styrene block copolymer, for example, which have been used as base polymers in ordinary hot-melt adhesives are used in place of the hydrogenated block-copolymers the compatibility on heating and melting is inadequate and a hot-melt adhesive composition cannot be realized, but of course these polymers may be added to a composition of this invention within ranges where the characteristics of the invention are not lost. Furthermore, waxes, such as paraffin wax and micro-wax, low molecular weight polyethylene, or low molecular weight rubbers such as polybutene, polyisoprene, polyisobutylene and polybutadiene, or bulking oils such as the paraffin, naphthene and aromatic hydrocarbon based petroleum distillation fractions as well as liquid rosin and liquid terpenes, or aggregates such as talc, silica, calcium carbonate and flowers of zinc, for example, can be added to a composition of this invention within ranges such that the characteristics of the invention are not lost. Moreover, antioxidants may be added to a composition of this invention in an amount preferably with the range of up to 3% with respect to the whole composition.

The hot-melt adhesive compositions in this invention can be obtained with such a constitution, but in consideration of the coating properties when melted, the melt viscosity of a composition of this invention preferably does not exceed 100,000 cps/200°C, and it is most desirably at least 1,000 cps/200°C but not more than 20,000 cps/200°C, and from the viewpoint of the required adhesion heat resistance, a composition with an R & B softening point of at least 100°C but less than 160°C is preferred, and a composition with an R & B softening point of at least 120°C but less than 160°C is most desirable.

Such compositions can be obtained as adhesives which are eminently suitable for melt-coating apparatus of the type known as a hot-melt applicator, but of course the adhesives obtained from compositions of this invention can be formed into sheets, or they can be used in methods where the adhesive is pre-coated on the adherends and then they are reheated and bonded.

## Method for the Production of an Adhesive

Adhesives comprising compositions of this invention can be produced using any of the methods generally used for the production of hot-melt adhesives such as the method in which the components are simultaneously or sequentially mixed in a melting tank known as a heated-type fusion stirred tank by rotating the stirring paddles preferably under a current of nitrogen at a temperature generally of at least 150°C but not more than 250°C, the method in which the components are mixed while applying a shear while being heated using twin-rotating paddles in apparatus known as a kneader, or the method in which the materials are melt mixed with heating in an extruder, which is to say with a single or twin screw.

### Action

The hot-melt adhesives which contain the three components of this invention, as a result of the co-presence of the three components, provide adhesives which have excellent adhesion heat resistance on polyolefin resins and especially polypropylene, where adhesion has been a problem, and on metals, and, moreover, these adhesives have excellent stability on heating when being melted for use in melt coating apparatus, and there is little resin tack after bonding and so they can be used very effectively even in applications where the adhesive is exposed, and the excellent action of the invention is achieved principally by the conjoint use of these three components.

### Examples and Comparative Examples

#### Methods of Evaluation

R & B Softening Point: Measured in accordance with JIS K 2207

Melt Viscosity: Measured by heating to 190°C using a B-type rotating viscometer in accordance with JAI 7 1980

Melt Stability: Melted at 190°C in a Nodoson Model XI hot-melt applicator (manufactured by the Nodoson Co.) and the presence of absence of separation in the tank was checked after 5 hours.

The results were evaluated on the basis of the following criteria:

O: No separation at all was seen

X: Unusable because of separation

The presence or absence of adhesion due to heating was checked at the same time and evaluated on the basis of the following criteria:

O: No change from the original state

X: Pronounced change from the original state.

**Adhesive Strength:** The adhesive composition was introduced into the aforementioned applicator and, after 2 hours, it was coated at a rate of 5 g/m in the form of lines onto a 10 cm<sup>2</sup> sheet of polypropylene film (300 µ) and then another sheet of polypropylene film (300 µ) was stuck on the top immediately using hand pressure. The bonded sample was cut to a width of 25 mm and the T-peel strength was measured. The measurements were made at room temperature (23°C) and at 80°C.

The tensile shear strength was measured in the same way by superimposing bonding parts of width 10 mm and measuring the strength while applying a shear of width 25 mm. Bonded samples were prepared in the same way but using aluminium sheets (100 µ) and the strengths were also measured using these samples. The T-peel strength was measured at a tensioning date of 200 mm/min, and the strength obtained is indicated in units of kgf/25 mm. The tensile shear strength was measured at a tensioning date of 10 mm/min and the strength obtained is indicated in units of kgf/10 mm lap x 25 mm.

The creep temperature was measured using the softening temperature measurement method for adhesives of JIS K 6844 and, using a bonded sample of the same type as the aforementioned samples used for measuring the tensile shear strength, a load of 200 g was applied to the bonded part of width 25 mm x 10 mm lap and the temperature was raised at a rate of 2°C at 5 minute intervals after maintaining the sample at 38°C for 15 minutes in a constant temperature container and the result is indicated as the temperature at which the bonded part failed.

#### **Examples 1 to 6 and Comparative Examples 1 to 5**

Viscol 660P (Sanyo Kasei Co.) (1.12 kg), 1.12 kg of Vistack L (Chiba Fine Chemical Co.) and 40 g of antioxidant Irganox 1010 (high molecular weight hindered polyhydric phenol, Ciba-Geigy Co.) were melted and stirred in a 10 litre capacity stirred tank which had been heated to 200°C and, after achieving dissolution 1.12 kg of viscous

tackifier YS Polystar-T-145 (terpene-phenol resin, softening point 145°C, Yasuhara Yushi Co.) were added gradually and, after raising the liquid temperature to 200°C, 0.6 kg of the copolymer Clayton G-1657 were added and the mixture was stirred for 2 hours and, after confirming that dissolution had occurred, the material was discharged from the tank and an adhesive was obtained. The results obtained on evaluation using the methods outlined above as shown in the tables as Example 1.

Adhesives were prepared in the same way but changing the tackifier of Example 1 to either Quinton G-100 (C<sub>6</sub>-based petroleum resin, softening point 95°C, Nippon Zeon Co.) or Alkon P-115 (hydrogenated petroleum resin, softening point 115°C, Arakawa Kagaku Co.) in Examples 2 and 3, changing the ratio of the components of Example 1 in Example 4, and with an adhesive obtained from copolymer, YS Polystar T-145 as the tackifier and Viscol 660P as the crystalline polypropylene as Example 5.

As comparative examples, either no copolymer was used or Kariflex TR-1107 (styrene-isoprene-styrene copolymer, Shell Chemical Co.), EV-420 (EVA, Mitsui Polychemical Co.), A-704 (EEA, Mitsui Polychemical Co.) were used instead of the copolymer in Example 1, or non-crystalline Vistak was used for the polypropylene in Comparative Examples 1 to 5 respectively. The method of preparation was just the same as in Example 1. The component ratios are shown in the tables.

Moreover, the polyamide-based hot-melt adhesive DPX-850 (Henkel Shiromizu Co.) was used for Comparative Example 6.

The results of the various evaluations are shown in the tables.

**Table**

Component, WI% (Trade Names)	Example 1	Example 2	Example 3	Example 4	Example 5	Comp.Ex. 1	Comp.Ex. 2	Comp.Ex. 3	Comp.Ex. 4	Comp.Ex. 5	Comp.Ex. 6
Clayton G-1657	15	15	15	28	24.5						33
Kariflex TR-1107						15					
EVA EV-420							15				
EEA A-704								15			
Polyamide DPX-850									15		
Quinton C-100		28								15	
YS Polystar	28			28	49	33		28	28		
T-145			28				28		28		33
Aikon P-115				28							
Viscol 660P	28	28	28	15	24.5	33	28	28	28		
Vistarion										33	
Vistack L	28	28	28			33	28	28	28		
Irganox 1010	1	1	1	1	2	1	1	1	1	1	1

**Table (Continued)**

			Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Comp.Ex. 2	Comp.Ex. 3	Comp.Ex. 4	Comp.Ex. 5	Comp.Ex. 6
R&B Softening Point		°C	145	142	145	140	143	145	146	145	145	110	155
Melt Viscosity	CPS-190°C		3000	2500	3000	20000	23000	500	1000	500	500	25000	800
Melt Stability	Separation	O	O	O	O	O	O	X	X	O	O	O	O
	Coloration	O	O	O	O	O	O	△	O	O	O	O	X
Adhesive strength with polypropylene	Peel Strength	23°C	2.0	6.0	10.0	4.0	5.0	About 0	0.5	About 0	About 0	6.0	About 0
	Shear Strength	23°C	1.0	2.0	2.5	2.0	2.0	About 0	About 0	About 0	About 0	0.5	About 0
	Creep Temp.	80°C	50	30	45	60	50	About 0	5.0	About 0	About 0	25	About 0
		80°C	10	8	10	10	20	About 0	About 0	About 0	About 0	2	About 0
		130°C	120°C	125°C	115°C	120°C	Could not be measured	40°C	Could not be measured	90°C	Could not be measured	90°C	Could not be measured
Adhesive strength with aluminium	Peel Strength	23°C	3.0	7.0	10.0	4.0	8.0	About 0	1.0	About 0	About 0	9.0	0.5
	Shear Strength	23°C	1.0	1.0	2.0	1.0	3.0	About 0	About 0	About 0	About 0	0.5	About 0
	Creep Temp.	80°C	70	30	40	45	60	About 0	6.0	About 0	About 0	30	21
		80°C	7	10	10	8	20	About 0	45°C	About 0	About 0	5	10
		120°C	115°C	120°C	115°C	125°C	Could not be measured		Could not be measured	80°C	Could not be measured	80°C	110°C

(c) Effect of the Invention

With an adhesive composition of this invention the adhesion properties and adhesion heat resistance on olefin-based resins and especially polypropylene which have been a problem with conventional adhesives as well as on metals are excellent and, moreover, it is possible to provide hot-melt adhesives which have excellent melt stability in the melt coating bonding method with a hot-melt applicator known as product assembly, and these give excellent results when used effectively in various bonding fields such as the bonding and sealing of electrical parts, automobile parts, and industrial filters.

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